NATIONAL ADVISORY COMMITTEE
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TECHNICAL NOTE 3405

TEMPERATURE-COMPOSITION LIMITS OF SPONTANEOUS

EXPLOSION FOR NINE ALKYLSILANES WITH AIR

AT ATMOSPHERIC PRESSURE

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ALKYLSILANES WITH AIR AT ATMOSPHERIC PRESSURE

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SUMMARY

To provide safe-handling information, the spontaneous explosion limits of nine alkylsilanes were determined as a function of temperature and fuel-air composition at a pressure of 1 atmosphere. Over a fuel concentration range of about 2 to 9 percent by volume in dry air, the fuels studied were nonexplosive below the following temperatures: tetramethylsilane $(CH_3)_4Si$, 450° C; trimethylsilane $(CH_3)_3SiH$, 300° C; diethylsilane $(C_2H_5)_2SiH_2$, 255° C; dimethylsilane $(CH_3)_2SiH_2$, 220° C; ethylsilane $(C_2H_5)SiH_3$, 215° C; isobutylsilane $(\underline{i}-C_4H_9)SiH_3$, 200° C; n-butylsilane $(\underline{n}-C_4H_9)SiH_3$, 185° C; methylsilane $(CH_3)SiH_3$, 125° C; and vinylsilane $H_2C=CH-SiH_3$, 90° C. Although the explosion temperatures apply only to the apparatus used herein, it seems very probable that these silanes can be safely handled in the gas phase at room temperature without danger of a spontaneous reaction. Since the explosion temperatures of the alkylsilanes are lower than those of analogous hydrocarbons (500° to 600° C) and decrease as hydrogen atoms are substituted for methyl groups, it appeared that the Si-H bond is more readily susceptible to oxidation than the C-H bond.

INTRODUCTION

Combustion properties of hydrocarbon fuels such as flame speed, flammability limit, ignition energy, and quenching distance have been extensively investigated. For certain combustion processes, it is desirable to employ fuels that have more favorable combustion characteristics than the hydrocarbons, but that possess similar physical properties. A class of compounds which might meet these requirements is the alkylsilanes. Consequently, several alkylsilanes were synthesized at the NACA Lewis laboratory; their physical properties (such as boiling point, melting point, heat of combustion, etc.) are reported in reference 1. At the time these silanes were synthesized, the conditions under which they could be safely handled and stored, particularly in contact

with air, were unknown. The present report describes a study directed
toward establishing the conditions of temperature and concentration in
dry air that will permit safe handling of this class of fuels.

Methyl-, dimethyl-, trimethyl-, tetramethyl-, ethyl-, diethyl-,
n-butyl-, isobutyl-, and vinylsilanes were investigated in this study.
Premixed fuel-air mixtures, with the silane concentration ranging from
about 2 to 10 percent by volume, were admitted to a heated, evacuated
reaction vessel to a pressure of 1 atmosphere; and the lowest tempera-
ture at which explosion would occur was then determined. The explosion
region of the nine alkylsilanes as a function of temperature and fuel-
air composition was therefore established. A comparison of the explosion
region of the alkylsilanes with the hydrocarbon compound that would result
by replacing the silicon atom with a carbon atom was made wherever
possible.

APPARATUS AND PROCEDURE

Fuels. - All the fuels used in this study were prepared by reduc-
tion of the proper alkylchlorosilane with lithium aluminum hydride in
anhydrous ethyl ether or dioxane as described in reference 1. Original
purity was estimated to be 95 percent or greater.

Procedure. - A diagram of the apparatus used for determining the
spontaneous explosion limits of the alkylsilanes is shown in figure 1.
Fuel and dry air were admitted at the positions indicated and mixed in
a 1-liter storage bulb by means of a magnetic stirrer. The pressure of
the mixture in the storage bulb was such that, when opened to the heated
reaction vessel, the resulting pressure was 1 atmosphere. If an explosive
reaction occurred before the pressure in the reaction vessel reached 1
atmosphere, or if no explosion took place at 1 atmosphere, the reaction
vessel was evacuated and the temperature decreased or increased accord-
ingly. The temperature of the pyrex reaction vessel, $1\frac{1}{2}$ inches in diam-
eter and $10\frac{1}{2}$ inches in length, was measured using a thermocouple attached
to the outside of the vessel.

Admission of the mixture to the reaction vessel was usually made as
rapidly as possible although, as described later, the mixture was some-
times admitted very slowly to determine the presence of cool flames.
Occurrence of an explosion was indicated by a surge of the mercury
in the manometer, and occasionally a flame was seen to travel up the tube
leading from the reaction vessel. Although such flames usually did not
travel very far, they did on several occasions flash back into the mixing
bulb and cause a serious explosion. Consequently, a roll of wire gauze
was placed between the mixing bulb and the reaction vessel to serve as a
flame trap. After this flame arrester was installed, no further trouble
was encountered from flash back.

The minimum temperature for explosion was determined within 15° C for various fuel-air mixtures of each given fuel. These minimum temperatures delineate the region of explosion and nonexplosion with respect to temperature and composition.

RESULTS AND DISCUSSION

The explosion limit curves for the nine fuels studied are presented in figure 2, and are summarized in figure 3. In this investigation, two distinctly different types of explosion limit were encountered. The first type, typical of those reported for hydrocarbons at a pressure of 1 atmosphere, was found for tetramethyl-, trimethyl-, and diethylsilane. In the case of these three fuels, the fuel-air mixture was admitted rapidly to the evacuated reaction vessel to a pressure of 1 atmosphere, and at a sufficiently high temperature an explosion occurred. The explosion usually occurred within 30 seconds after admission. If no rapid reaction took place in this length of time, only a very slow increase in the pressure was observed and no explosion was later detected even after time intervals of 1 hour.

The temperature-composition curves delineating the spontaneous explosive region for tetramethyl-, trimethyl-, and diethylsilane over a fuel-concentration range from about 2 to 10 percent are shown in figures 2(a) and (c). Determinations were made of both the temperature at which explosion occurred in 15 seconds or less and the temperature below which no explosive reaction occurred. As shown in figures 2(a) and (c), these two temperatures differ by less than 15° C; and, consequently, the minimum explosion temperature under the conditions of the test lies within this 15° C temperature range.

A second type of explosion limit was encountered for dimethyl-, methyl-, ethyl-, n-butyl-, isobutyl-, and vinylsilane. The temperature-composition curves for these compounds could not be obtained by the technique just described. The temperatures below which no explosion occurred, shown in figures 2(b) and (c), could be determined unambigously. Above these temperatures, however, the observed phenomena depended upon the rate of admission of the fuel-air mixture to the reaction vessel. In those cases where the mixture was introduced rapidly, an explosion took place before the pressure in the reaction tube reached atmospheric pressure. Mixtures were therefore admitted very slowly to observe the pressure at which reaction was first indicated. By this procedure it was observed that a series of minor explosions, probably cool flames, occurred over a pressure range of 50 to 100 millimeters of mercury. These were recorded as explosions. After this pressure range was exceeded, no further reaction took place when the mixture was slowly admitted to a pressure of 1 atmosphere at temperatures just above the nonexplosion temperature.

Since a very vigorous reaction took place when the mixture was rapidly admitted, it is believed that the cool-flame reaction occurring at a pressure of 50 to 100 millimeters set off an explosive reaction when additional fuel-air mixture was supplied at a sufficiently rapid rate. The temperature-composition explosion curve for methyl-, dimethyl-, ethyl-, n-butyl-, and isobutyl-, and vinylsilane (figs. 2(b) and (c)) actually represent the appearance of cool flames. The cool flames are capable of causing an explosion if additional fuel-air mixture is immediately available to react. If cool flames did not occur, the explosion temperature for the mixtures at an initial pressure of 1 atmosphere would be expected to be higher than the temperatures recorded in figures 2(b) and (c) for the occurrence of cool flames.

For rich mixtures, the explosion temperatures of ethyl-, n-butyl-, and isobutylsilane were 215°, 185°, and 200° C, respectively. Since the range of experimental error may be as great as ±20° C, the explosion limits of these three fuels can probably be considered the same. This represents an increase in explosion temperature of about 80° over methyl-silane (see fig. 3). Since monosilane.(SiH_4) is spontaneously flammable at room temperature (ref. 2), the addition of one methyl group in methyl-silane appreciably reduces the reactivity. It appears that the addition of a side chain of two carbon atoms ($C_2H_5SiH_3$) reduces the reactivity of the molecule as compared with a side chain of one carbon atom (CH_3SiH_2). However, further increases in the length of the side chain to four carbon atoms, (butylsilanes) produces only a very small change in the reactivity. If the side chain is unsaturated as in vinylsilane ($H_2C=CH-SiH_3$), the reactivity appears greater than for either ethyl- or methylsilane. Vinylsilane is the only compound with a positive heat of formation among the silanes studied (ref. 1).

In figure 4 are presented the temperature-composition explosion curves for several hydrocarbon compounds as given in references 3 to 6. The spontaneous explosion limit curves for the hydrocarbons fell between 500° and 600° C. The temperature-composition explosion curves for the alkylsilanes are similar to those of the hydrocarbons, but occur at appreciably lower temperatures. As shown in figure 4, the explosion curves of the hydrocarbons show little variation with changes in fuel structure. A marked separation in explosion temperatures was observed among members of the alkylsilane series. As shown in figure 3, the five fuels possessing three Si-H bonds have the lowest explosion temperature. As the number of Si-H bonds is reduced, the temperature required for an explosive reaction is increased. For tetramethylsilane where no Si-H bonds are present, the explosion temperature approaches that of the hydrocarbons.

Since the explosion temperature is lower for the alkylsilanes than for the hydrocarbons and since it decreases as hydrogen atoms are substituted for methyl groups, it appears very probable that the Si-H bond

is more readily subject to oxidation than the C-H bond. This conclusion might also have been reached by considering the theoretical bond-strength calculations of reference 7, which show the strength of the Si-H bond to be appreciably weaker than that of the C-H bond.

In reference 8, it is proposed that oxidation reactions of the hydrocarbons proceed by free radicals. To permit the formation of these radicals, the first step in the oxidation must involve the vulnerability of the molecule to bond-breaking reactions. It was proposed in reference 8 that radicals are first formed by removal of a hydrogen atom from the molecule, which is then subject to attack by addition of O_2 to the free carbon valence. A general over-all scheme starting with a free radical R can therefore be presented as follows (ref. 9):

$$R \xrightarrow{O_2} ROO \xrightarrow{RH} ROOH + R \tag{1}$$

The fact that the alkylsilanes oxidize more readily than the hydrocarbons, and that hydrogen atoms can be removed more readily from the silanes, would lend support to the initial step proposed for the hydrocarbon oxidation, namely, the removal of a hydrogen atom. If the silane oxidation then follows the mechanism of the hydrocarbon oxidation, the scheme presented in equation (1) might also be adopted.

In regard to safe handling, vapor phase mixtures of the most reactive fuel studied are nonexplosive below about 90° C; consequently, even though these results strictly apply only to the conditions and apparatus geometry used, when handled at room temperature (60° or 70° C lower than the lowest explosion temperature) the probability of spontaneous explosion from these fuels is extremely small.

SUMMARY OF RESULTS

In an investigation of the explosion limits of nine silanes as a function of temperature and concentration at a pressure of 1 atmosphere, the following results were obtained:

1. Over a fuel concentration range of 2 to 9 percent by volume in dry air, the fuels studied were nonexplosive below the following temperatures: tetramethylsilane $(CH_3)_4Si$, 450°; trimethylsilane $(CH_3)_3SiH$, 300°; diethylsilane $(C_2H_5)_2SiH_2$, 255°; dimethylsilane $(CH_3)_2SiH_2$, 220°; ethylsilane $(C_2H_5)SiH_3$, 215°; isobutylsilane $(i\text{-}C_4H_9)SiH_3$, 200°; n-butylsilane $(\underline{n}\text{-}C_4H_9)SiH_3$, 185°; methylsilane $(CH_3)SiH_3$, 125°; and vinylsilane $H_2C\text{=}CH\text{-}SiH_3$, 90° C. The large variation in explosion temperatures among the silanes indicated that, substituting hydrogen atoms for the methyl groups attached to the silicon atom decidedly increased their reactivity.

2. Although the reactivity of the silanes studied appeared greater than for analogous hydrocarbons, which had spontaneous explosion temperatures between 500° and 600° C, it appears very probable that even the vapors of the most reactive fuel studied can be safely handled in dry air at room temperature.

3. Since the explosion temperature was lower for the alkylsilanes than for the hydrocarbons and since it decreased as hydrogen atoms were substituted for methyl groups, the Si-H bond is probably more susceptible to oxidation than the C-H bond.

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    National Advisory Committee for Aeronautics
        Cleveland, Ohio, December 17, 1954

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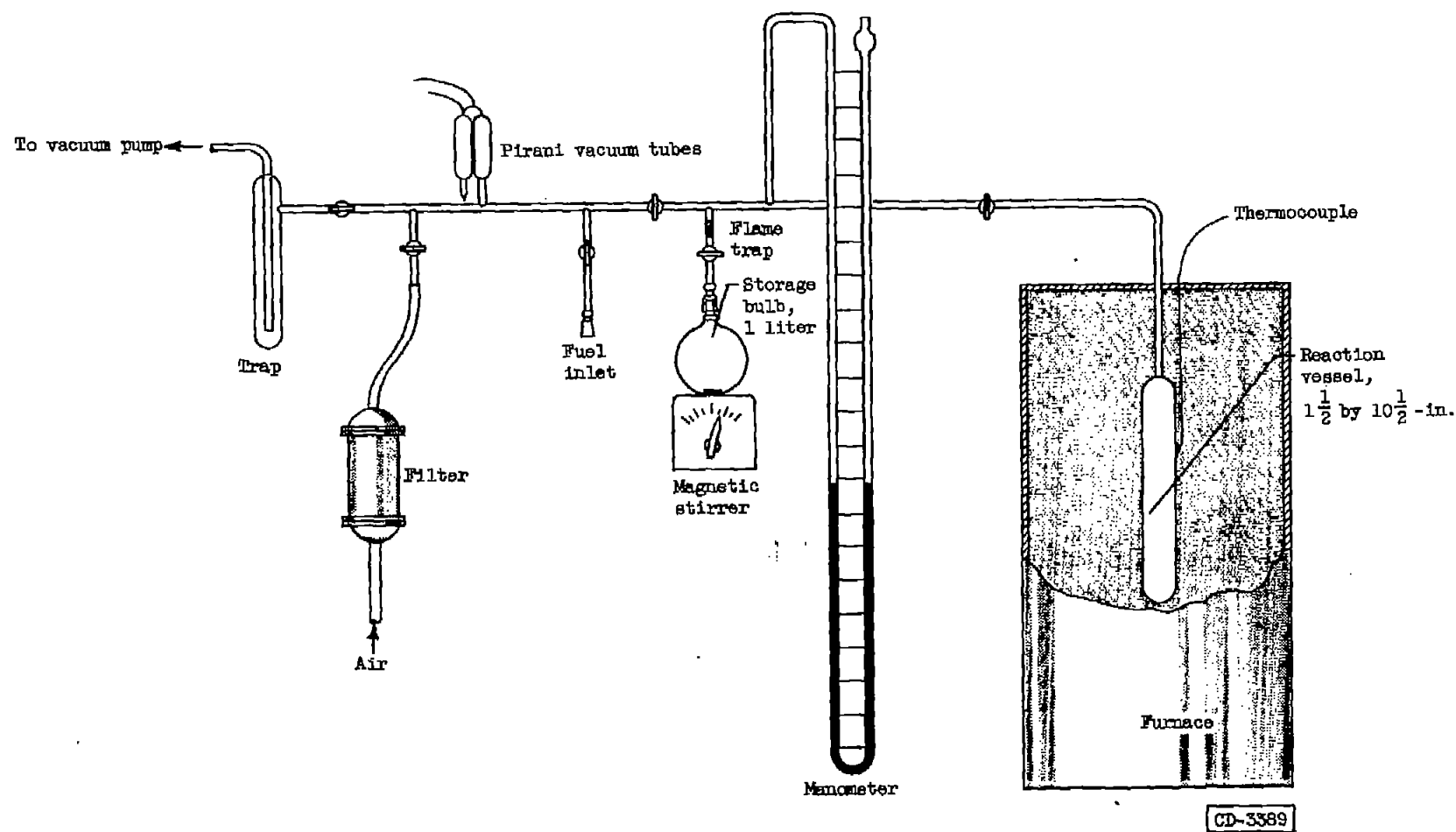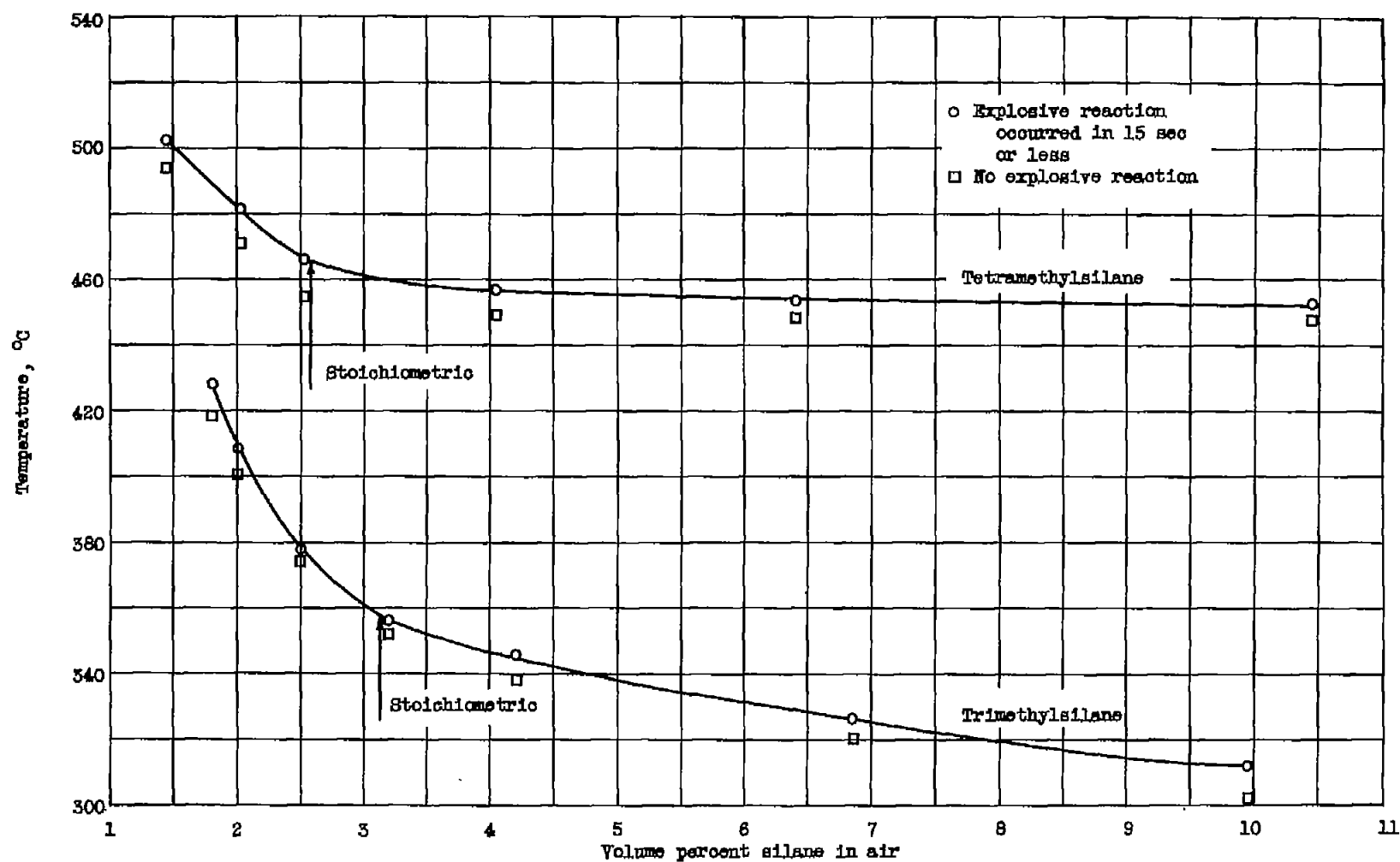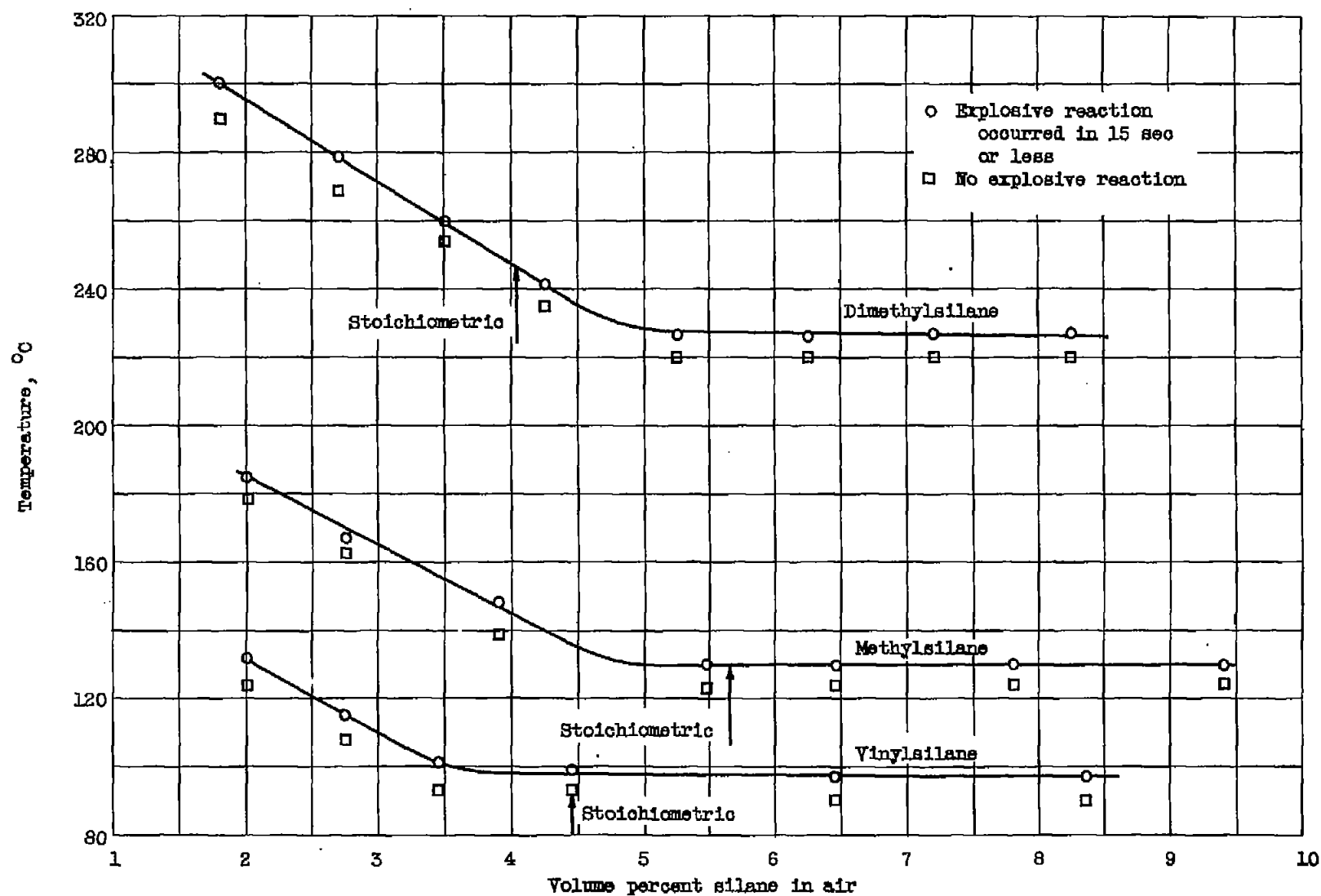
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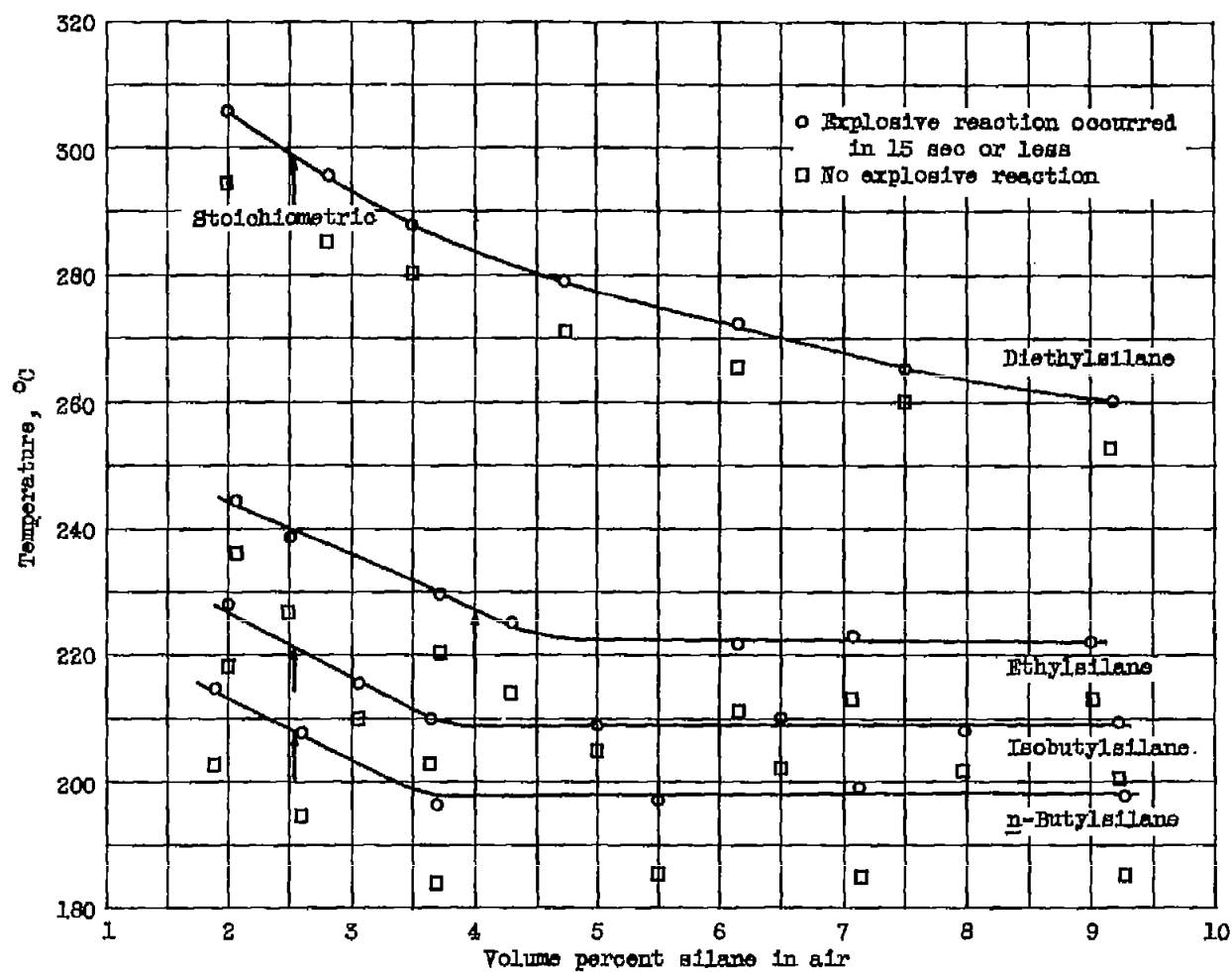Figure 1. - Apparatus for determining explosion limits.

(a) Tetramethyl- and trimethylsilanes.

Figure 2. - Temperature-composition explosion curves for alkylsilanes at pressure of 1 atmosphere.

(b) Dimethyl-, methyl-, and vinylsilanes.

Figure 2. - Continued. Temperature-composition explosion curves for alkylsilanes at pressure of 1 atmosphere.

(c) Diethyl-, ethyl-, isobutyl-, and n-butylsilanes.

Figure 2. - Concluded. Temperature-composition explosion curves for alkylsilanes at
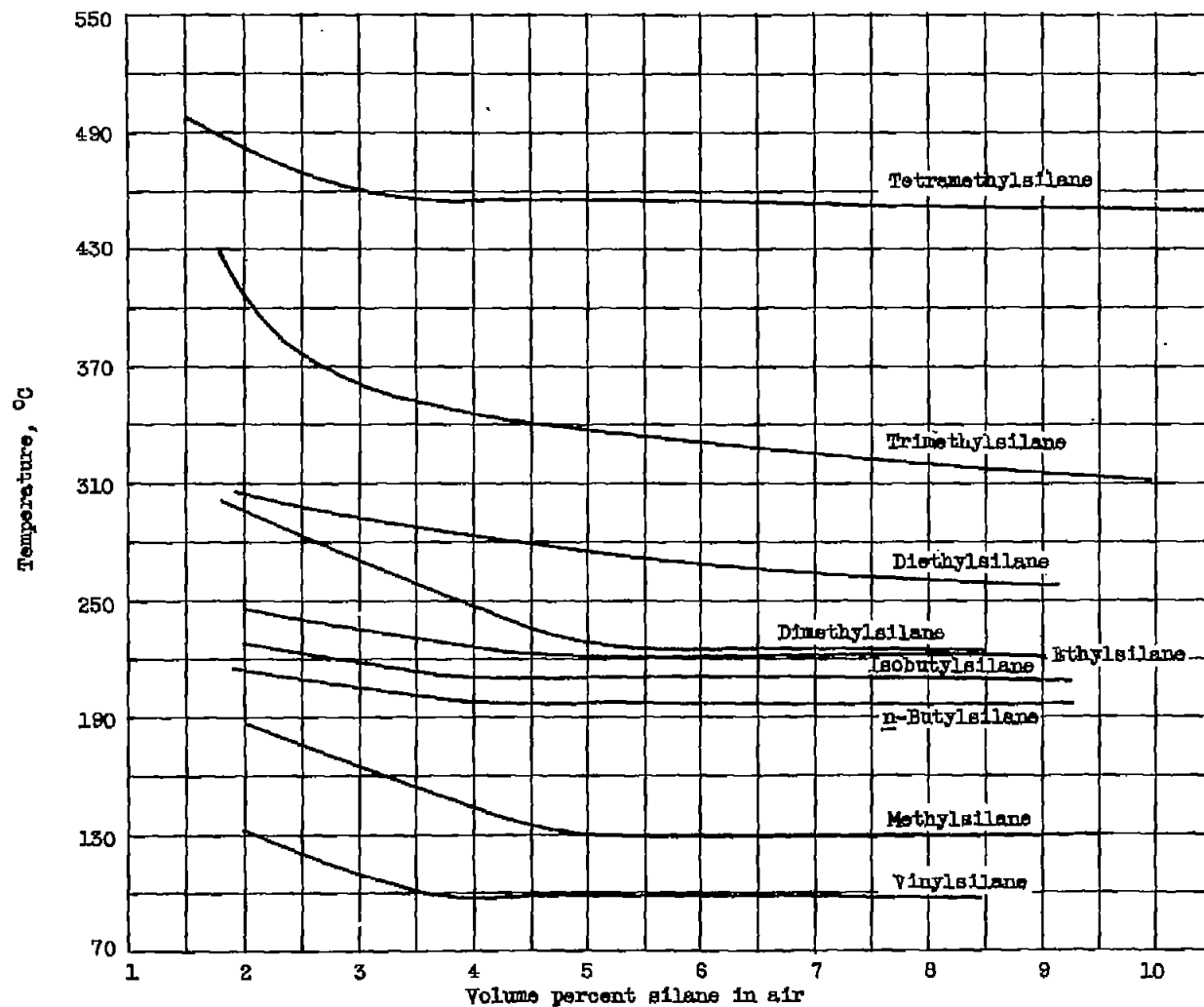pressure of 1 atmosphere.

Figure 3. - Summary of temperature-composition explosion curves for alkylsilanes at pressure of 1 atmosphere. Explosions occurred in 15 seconds or less.
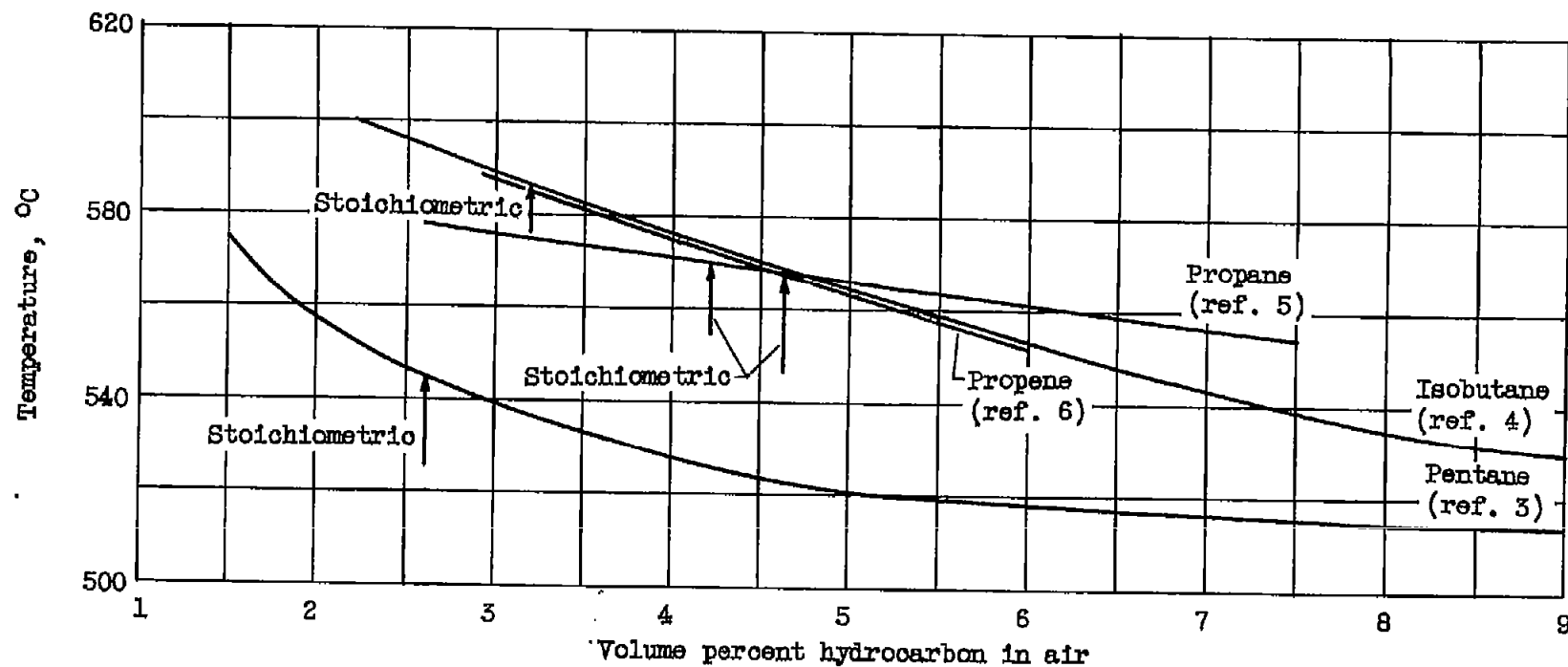
Figure 4. - Temperature-composition explosion curves for hydrocarbons at pressure of 1 atmosphere.